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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 2, 1979	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER (rept. no. 2)
4. TITLE (and Subtitle) "Loss of Lattice Rigidity in Austenite"		5. TYPE OF REPORT & PERIOD COVERED Technical Oct. 1978 – Sept. 1979
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Nicholas DeCristofaro* and Roy Kaplow		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0171
9. PERFORMING ORGANIZATION NAME AND ADDRESS Massachusetts Institute of Technology Cambridge, MA 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217		12. REPORT DATE 2 August 1979
		13. NUMBER OF PAGES 6 pages
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Unlimited

LEVEL II

DDC

RECEIVED
AUG 29 1979
C

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

To be published in Proceedings of ICOMAT-79, MIT, June 25-29, 1979.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Austenite, lattice instability, iron-nitrogen, Mössbauer spectroscopy, lattice excitation.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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S/N 0102-014-6601

Allied Chemical Corporation, Morristown, NJ 07960.

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LOSS OF LATTICE RIGIDITY IN AUSTENITE

Nicholas DeCristofaro and Roy Kaplow

Massachusetts Institute of Technology

TECHNICAL REPORT No. 2, 1979

August 2, 1979

to

The Office of Naval Research

Contract No. N00014-76-C-0171, NR031-795

To be published in

ICOMAT-79, Proceedings, June 25-29, 1979

M.I.T., Cambridge, Massachusetts

79 08 27 117

Loss of Lattice Rigidity in Austenite*

Nicholas DeCristofaro[†] and Roy Kaplow[††]

Mössbauer spectra were taken at and below room temperature in iron -2.4 wt.% nitrogen samples containing various amounts of stabilized martensite and austenite ($M_s \simeq 260K$). The intensities of the martensite spectra increase with decreasing temperature as expected from the normal thermal variation of the recoilless fraction. Conversely, the intensities of the austenite spectra are smaller below room temperature and M_s, and decrease with decreasing temperature. This corresponds to a decreasing recoilless fraction, which is associated with a lessening of lattice resistance to excitations caused by the transference of the gamma-ray recoil momentum. This behavior is thought to be related to lattice instabilities in the austenite phase, possibly related to its transformation to martensite. The magnitude of the effect indicates that, although the excitations in themselves may be localized, these instabilities are characteristic of the bulk material and cannot be explained in terms of the conventional theory of pre-existing martensitic embryos.

I. Introduction

Recently, the concept that various crystal lattices become structurally unstable on cooling has assumed an important role in models for martensitic or displacive transformations. In this context, a number of anomalous effects occurring in the parent (austenite) phase at temperatures above M_s have been reported. Electron microscopic effects [1-5], softening of elastic constants [6,7], and resistivity and magnetic anomalies [8,9] have been observed. Mössbauer studies of Fe-Ni and Co-Fe systems [10-12] show a decrease in the recoilless fraction of the parent phase as the temperature is lowered to M_s. It has been argued that these "premartensitic phenomena" intensify as the temperature is lowered to M_s [1] and continues to exist in the retained austenite at temperatures below M_s [13].

These effects have been associated with the martensitic transformation in a variety of ways. Models exist in which specific phonon modes in the parent phase related to the martensitic structure [14,15] become unstable and eventually trigger the transformation through their own stress fields [16-18]. Other interpretations speculate two step processes including either the slight distortion of the parent lattice [5] or the precipitation of a transitory phase [3,4] preceding the actual transformation. In many instances, the model for martensitic trans-

formation involves inhomogeneously distributed "embryos" based on (a) spatially localized, "soft" vibrational modes [19], (b) static atomic displacement waves [10], or (c) particular configurations of defects (e.g. dislocations) [21].

II. Experimental Procedure

Samples of iron 2.4 wt.% nitrogen (8.9 at.%) austenite (M_s approximately 260°K) [22] were produced by nitriding iron foil (0.025 mm thick) in flowing mixtures of NH_3 and H_2 at 973°K and rapidly quenching directly from the nitriding atmosphere.

Mössbauer spectra were measured on a constant acceleration spectrometer with a gamma-ray source of [57]Co embedded in a copper matrix. The austenite absorber was mounted in a low-temperature dewar on this spectrometer so that its temperature could be controlled in situ, without disturbing the source-sample-detector geometry.

The austenitic sample was cycled a number of times between room temperature (295°K) and 183°K. The total time spent at 183°K exceeded 24 hours and the total time at room temperature following the first quench exceeded one week. This process served to ensure that the martensite formed was stabilized both in amount and with respect to short term room temperature aging for this temperature range. The first data set, following this treatment, comprised a sequence of Mössbauer measurements at 295, 183 and 295°K. The spectrum recorded at room temperature is illustrated in Figure 1; it indicates the presence of approximately 40% martensite (the complex, spectrum labeled M), and 60% austenite, (the spectrum labeled A).

The sample was then quenched to 82°K and cycled between this temperature and room temperature in a manner similar to that described above. Following this treatment, another series of Mössbauer spectra were recorded at 295, 183, 82 and 295°K. The spectrum measured at room temperature indicated that during the additional cooling from 183°K to 82°K, the amount of martensite increased to approximately 55%.

III. Analysis of Mössbauer Spectra

The recoilless fraction, which determines the absolute magnitude of the relevant spectra, is related to a recoil energy, R, that would be transferred to a single free and motionless atom when its nucleus absorbs a gamma-ray, and to the effective, quantized energy increment for available lattice excitations, E*, in the form: [23]

$$f_T = \exp(-R/E*) \tag{1}$$

For the vibrational excitation of a Debye solid:

$$E* = (1/6)\, k_B\, \theta_D / \{1/4 + (T/\theta_D)^2 \int_0^{\theta_D/T} \frac{x\,dx}{e^x - 1}\} \tag{2}$$

2

where k_B is Boltzmann's constant, θ_D the Debye characteristic tempera-
ture, and T the absolute temperature. On the basis of ordinary temper-
ature-dependent vibrational behavior, the recoilless fraction should in-
crease with decreasing temperature. This temperature dependence, ex-
pressed in terms of f_T/f_{295}, predicted by Equation (1) and (2), is il-
lustrated as the solid curve in Figure 2. The value of $\theta_D \sim 411°K$, taken
as an average and from interpolation and extrapolation of various data
[24,25] is appropriate for both phases.

The theoretical intensity of a Mössbauer absorption peak, $P_{th}(E_s)$,
is related to the recoilless fraction, f_T, through the convolution: [26]

$$P_{th}(E_s) = \int_{-\infty}^{\infty} I(E, E_s) [1 - \exp(-f_T n \sigma(E))] \qquad (3)$$

where $I(E,E_s)$ is the nominally Lorentzian energy distribution of the
gamma-ray source, n is the effective thickness of the absorber in nuclei
per cm^2, and $\sigma(E)$ is the cross section for resonant absorption. In
practice, the proper absorption intensities and shapes are obtained
through the convolution of the theoretical intensity with a Gaussian
curve to compensate for instrumental broadening [17]. Since the nuclear
parameters are constant, the temperature variation of the magnitude of
resonant absorption in each phase is dependent only on f_T.

When the argument of the exponential term in Equation (3) is small,
the depth of the Mössbauer peaks is also small and may be approximated as
being directly proportional to f_T. This is the case for the ferromagne-
tic martensite spectra. For the austenite spectrum, where the exponent
is larger, the more rigorous nonlinear treatment of Equation (3) must be
applied.

IV. Experimental Results

The first series of Mössbauer measurements, on 40% martensite sta-
bilized at 183°K, were recorded at 295, 183 and 295°K again. The marten-
site peaks showed increased intensity at the low temperature by the a-
mount expected from the thermal increase in f_T. The austenite peak,
however, showed a decrease in intensity corresponding to a decrease in f_T
of approximately 9%.

The second series of measurements, on 55% martensite stabilized at
82°K, were recorded at 295, 183, 82 and 295°K again. As in the first
series, the martensite peaks were observed to increase with decreasing
temperature in the expected manner while the austenite showed a contin-
uous decrease in f_T with decreasing temperature. In both series of mea-
surements, all peaks returned to their original room temperature inten-
sities when the sample was reheated to 295°K.

The measured relative recoilless fractions are compared to the theo-
retical values in Figure 2. An important aspect of these results is that
the f_T value for austenite at 183°K is the same, within precision, for
both series of measurements.

IV. Discussion

The reduced value of the recoilless fraction in the austenite at low temperature implies an increase in the probability that a gamma-ray will create a lattice excitation, i.e., that it will be absorbed in a non-recoilless manner. This increasing probability reflects a lessening of lattice resistance to excitation. The energy available from the gamma-ray to create an excitation is, at most, the free atom recoil energy, R. R is determined by the gamma-ray energy and the atomic mass of the atom, and equals 3.1348×10^{-15} joules (1.9567×10^{-3} ev) for the Mössbauer transition in ^{57}Fe [28]. This value is an order of magnitude less than thermal energy at room temperature.

Since at temperatures below M_s there is a driving energy for the transformation of austenite to martensite which increases with decreasing temperature, such lattice excitations formed in the austenite structure might be related to the martensitic transformation. Without distinguishing between excitations in the form of static distortions or vibrational displacements (such as of soft normal modes) one can conceive of an excitation causing a localized change in the atomic configuration toward the martensitic structure. The behavior of the recoilless fraction of the austenite with decreasing temperature is consistent with such a proposition. The essential independence of the recoilless fraction of the austenite from both the amount of martensite already formed and the immediate tendency to form more martensite indicates that it is at least primarily an intrinsic property of the austenite. This does not necessarily mean that prior treatment (e.g., the formation of the additional amount of martensite at 82°K) does not change the excitation probability at all, but only that such effects (e.g., as may be due to strains, etc.) are small in comparison to the intrinsic effect.

If the localized excitations are normal vibrational modes enhanced by a lessening of certain elastic constants, a decreasing f_T would imply a decrease in the vibrational characteristic energy required to create the excitation (e.g., the Debye excitation energy given in Equation (2)). If the excitations are different from the normal modes and independent of them, the probability of a recoilless event would take the form:

$$f_T = f_N f_S \qquad (4)$$

where f_T is the measured recoilless fraction at temperature T, f_N is the probability that the gamma-ray absorption will not create a normal thermal excitation, and f_S is the probability it will not create a special excitation. If we assume that $f_S = 1$ at 295°K and f_N is the Debye value at all temperatures, the temperature variation of f_S and E^* can be estimated (where E^* is the characteristic energy associated with the special excitation and $f_S = \exp(-R/E^*)$). These values are given in Table I. Although the value E^*_S decreases with temperature the probability of such excitations existing through thermal effects, estimated through the Boltzman factor, $\exp(-E^*_S/kT)$, does not increase, since the thermal energy, kT, decreases more rapidly. If we were to assume that the austenite tendency toward instability onsets well above M_s the absolute values of the f_T's would be slightly lower. This alternate assumption has only

minor effects on the derived values.

The anomalous decrease in f_T, which amounts to 27% at 82°K, is too large to be explained in terms of localized instabilities at small metastable regions ("embryos") which are postulated to serve as nucleation centers for martensite. Based on estimates of their size (10^6 atoms) and density ($10^7/cm^3$)[29], "embryos" would comprise only 10^{-10} of the material. Even if all atoms in an "embryo" behaved as if $f_T = 0$, they could not in themselves cause the observed behavior. Thus, the loss of lattice rigidity in the austenite must be a bulk effect, reflecting the overall mechanical instability of this phase at low temperatures.

VI. Summary

The anomalously decreasing recoilless fraction of the austenite with decreasing temperature below ambient is associated with lattice instabilities of this phase, possibly related to its transformation to martensite. The magnitude of the effect indicates that, although the excitations themselves may be localized, they are characteristic of the bulk material and cannot be explained in terms of the conventional theory of pre-existing martensitic embryos. It is unknown whether the gamma-ray induced excitations are stable or unstable. However, in the course of each Mössbauer measurement, it is certain than an appreciable amount of additional martensite has not been formed.

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TABLE I: Estimated Values of f_S and E_S^*

T °K	f_T	f_D	f_S	E_S^* (joules)	$\exp(-E_S^*/kT)$
295	0.778	0.778	1.0	---	0.0
183	0.720	0.846	0.851	$1.95*10^{-14}$	0.463
82	0.661	0.901	0.734	$1.01*10^{-14}$	0.409

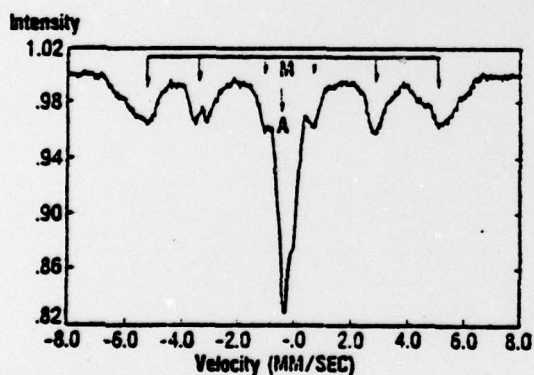FIGURE 1: 295°K Mössbauer Spectrum of Fe-2.4 wt.%N.

FIGURE 2: Temperature Dependence of the Recoilless Fraction; Debye Theory (—) and Experiment.